

United States Patent Application for:

**APPARATUS AND METHOD FOR CONTROLLED
APPLICATION OF REACTIVE VAPORS TO PRODUCE THIN
FILMS AND COATINGS**

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1 [0001] APPARATUS AND METHOD FOR CONTROLLED APPLICATION
2 OF REACTIVE VAPORS TO PRODUCE THIN FILMS AND COATINGS

3 [0002] This application is related to Provisional Application Serial No. 60/482,861,
4 filed June 27, 2003 and entitled: "Method And Apparatus for Mono-Layer Coatings";
5 Provisional Application Serial No. 60/506,846, filed September 30, 2003, and entitled:
6 ""Method Of Thin Film Deposition"; and, Provisional Application Serial No. 60/482,861,
7 filed October 9, 2003, and entitled : "Method of Controlling Monolayer Film Properties".
8

9
10 [0003] **BACKGROUND OF THE INVENTION**

11 [0004] 1. Field of the Invention

12 [0005] The present invention pertains to apparatus and a method useful in the
13 deposition of a coating on a substrate, where the coating is formed from chemically
14 reactive species present in a vapor which is reacted with the substrate surface.

15 [0006] 2. Brief Description of the Background Art

16 [0007] Both integrated circuit (IC) device fabrication and micro-electromechanical
17 systems (MEMS) fabrication make use of layers or coatings of material which are
18 deposited on a substrate for various purposes. In some instances, the layers are deposited
19 on a substrate and then are subsequently removed, such as when the layer is used as a
20 patterned masking material and then is subsequently removed after the pattern is
21 transferred to an underlying layer. In other instances, the layers are deposited to perform
22 a function in a device or system and remain as part of the fabricated device. There are
23 numerous methods for depositing a thin film layer or a coating, such as: Sputter
24 deposition, where a plasma is used to sputter atoms from a target material (commonly a
25 metal), and the sputtered atoms deposit on the substrate. Chemical vapor deposition,
26 where activated (e.g. by means of plasma, radiation, or temperature, or a combination
27 thereof) species react either in a vapor phase (with subsequent deposition of the reacted

1 product on the substrate) or react on the substrate surface to produce a reacted product on
2 the substrate. Evaporative deposition, where evaporated material condenses on a
3 substrate to form a layer. And, spin-on, spray-on, or dip-on deposition, typically from a
4 solvent solution of the coating material, where the solvent is subsequently evaporated to
5 leave the coating material on the substrate.

6 [0008] In applications where the wear on the coating is likely to occur due to
7 mechanical contact or fluid flow over the substrate surface on which the layer of coating
8 is present, it is helpful to have the coating chemically bonded directly to the substrate
9 surface via reaction of the species with the surface in order to obtain particular surface
10 properties.

11 [0009] With respect to layers and coatings which are chemically bonded to the
12 substrate surface, areas of particular current interest are those of integrated circuitry, and a
13 combination of integrated circuitry with mechanical systems, which are referred to as
14 micro-electromechanical systems, or MEMS. Due to the nanometer size scale of some of
15 the electrical devices formed, and the use of MEMS in applications such as the biological
16 sciences, where the type and properties of the coating on the substrate surface is used to
17 provide a particular functionality to the surface, a need has grown for improved methods
18 of controlling the formation of the coating or layer on the substrate surface. Historically,
19 these types of coatings were deposited in the liquid phase, resulting in limited film
20 property control and loss of device yield due to capillary forces. More recently, vapor-
21 phase deposition has been used as a way to replace liquid processing and to improve
22 coating properties.

23 [0010] For purposes of illustrating a few of the many potential applications for vapor
24 phase coatings, which must either be deposited to have particular critical properties and/or
25 to have particular permanent structural orientation relative to the underlying substrate,
26 applicants would like to mention the following publications and patents which relate to
27 methods of coating formation. Applicants would like to make it clear that some of this

1 Background Art is not prior art to the present invention because it has been published at
2 such a time that it is subsequent to the date of invention for applicants' invention. It is
3 mentioned here because it is of interest to the general subject matter.

4 [0011] Product applications employing coatings deposited on a substrate surface from
5 a vapor include the following, as examples and not by way of limitation. U.S. Patent
6 5,576,247 to Yano et al., issued November 19, 1996, entitled: "Thin layer forming
7 method where hydrophobic molecular layers preventing a BPSG layer from absorbing
8 moisture". U.S. Patent No. 5,602,671 of Hornbeck, issued February 11, 1997, which
9 describes low surface energy passivation layers for use in micromechanical devices. In
10 particular, an oriented monolayer is used to limit the Van der Waals forces between two
11 elements, reducing the attraction between the surfaces of the elements. An article by
12 Steven A. Henck in Tribology Letters 3 (1997) 239 -247, entitled "Lubrication of digital
13 micromirror devices", describes nearly fifty lubricants which were investigated for use in
14 a digital micromirror device. The lubricants included self-assembled monolayers
15 (SAMs), fluids, and solid lubricants. The lubricants were used to reduce the adhesion
16 between contacting surfaces within a microelectromechanical system (MEMS) device. In
17 an article entitled "Vapor phase deposition of uniform and ultrathin silanes", by Yuchun
18 Wang et al., SPIE Vol. 3258 - 0277-786X(98) 20 - 28, the authors describe uniform,
19 conformal, and ultrathin coatings needed on the surface of biomedical microdevices such
20 as microfabricated silicon filters, in order to regulate hydrophilicity and minimize
21 unspecific protein adsorption. Jian Wang et al., in an article published in Thin Solid
22 Films 327 - 329 (1998) 591 - 594, entitled: "Gold nanoparticulate film bound to silicon
23 surface with self-assembled monolayers, discuss a method for attaching gold
24 nanoparticles to silicon surfaces with a SAM used for surface preparation".

25 [0012] Patrick W. Hoffmann et al., in an article published by the American Chemical
26 Society, Langmuir 1997, 13, 1877 - 1880, describe the molecular orientation in
27 monomolecular thin organic films and surface coverage on Ge/Si oxide. A gas phase

1 reactor was said to have been used to provide precise control of surface hydration and
2 reaction temperatures during the deposition of monofunctional perfluorated alkylsilanes.
3 Although some process conditions are provided, there is no description of the apparatus
4 which was used to apply the thin films. T.M. Mayer et al. describe a "Chemical vapor
5 deposition of fluoroalkylsilane monolayer films for adhesion control in
6 microelectromechanical systems" in J. Vac. Sci. Technol. B 18(5), Sep/Oct 2000. This
7 article mentions the use of a remotely generated microwave plasma for cleaning a silicon
8 oxide substrate surface prior to film deposition, where the plasma source gas is either
9 water vapor or oxygen. U.S. Patent No. 6,203,505 to Jalisi et al., issued March 20 2001
10 describes guide wires having a vapor deposited primer coating. The guide wires are an
11 intraluminal device having an adhesive primer coat formed of a carbonaceous material
12 and a lubricious top coat of a hydrophilic polymeric material. One preferred coating
13 method for applying a carbon-based primer coating is chemical vapor deposition. The
14 coating is a plasma polymerized coating, so that the resulting polymer is an amorphous
15 structure having groups in the structure other than the monomer groups of the source
16 materials. For example, plasma polymerized polyethylene may include a variety of
17 functional groups, such a vinyl, in addition to the methylene groups. In their article
18 entitled: "Amino-terminated self-assembled monolayer on a SiO₂ surface formed by
19 chemical vapor deposition", J. Vac. Sci. Technol. A 19(4), Jul/Aug. 2001, Atsushi
20 Hozumi et al. describe the formation of self-assembled monolayers (SAMs) on n-type Si
21 (100) wafers which were photochemically cleaned by a UV/ ozone treatment, whereby a
22 thin SiO₂ layer was formed on the silicon surface. The SAM coating was applied by
23 placing a cleaned wafer together with a silane liquid precursor diluted with absolute
24 toluene into a container having a dry nitrogen ambient atmosphere. The container was
25 sealed with a cap and heated in an oven maintained at 373 °K.

26 [0013] International Patent Application No. PCT/US01/26691, published on April 11,
27 2002, describes substrates having a hydrophobic surface coating comprised of the reaction

1 products of a chlorosilyl group compound and an alkylsilane. In a preferred embodiment,
2 a hydrophobic coating is formed by the simultaneous aqueous vapor phase deposition of a
3 chloroalkylsilane and a chlorosilyl group containing compound to form an anchor layer,
4 which may then be capped with a hydrophobic coating. The reactants are said to be
5 vapor-deposited simultaneously in a closed humidity-controlled chamber. Dry air, humid
6 air, or dry air saturated with coating precursor vapor was introduced at one end of the
7 chamber and exhausted at the other. The reaction precursors are said to be introduced
8 into the reaction chamber by flowing dry air over the precursor liquid and into the
9 chamber. U.S. Patent No. 6,383,642 to Le Bellac et al., issued May 7, 2002 described
10 formation of a hydrophobic/oleophobic coating on a substrate such as a glass or plastic
11 material. The coating precursor is introduced into a chamber which employs a pulsed
12 plasma, with the frequency of the plasma generation source ranging from 10 kHz to 10
13 GHz at a power from 100 to 2000W, where the substrate surface area to be coated is 0.4
14 M². The precursors are introduced into the chamber at various flow rates to establish and
15 maintain a pressure in the chamber ranging from 0.1 to 70 Pa..

16 [0014] W. Robert Ashurst et al., discuss a method of applying anti-stiction coatings
17 for MEMS from a vapor phase in an article published by Elsevier Science B.V., in
18 Sensors and Actuators A 104 (2003) 213 - 221. In particular, silicon (100) samples cut
19 from a P-doped, n-type test wafer are rinsed in acetone and then cleaned by exposure to
20 UV light and ozone for 15 minutes. The samples are treated with concentrated HF for 10
21 minutes and then cleaned again as described above before introduction to a vapor
22 deposition chamber. In the vapor deposition chamber, the silicon substrates are
23 additionally cleaned of any organic contamination using an oxygen plasma which is
24 generated in the coating chamber, but at a sufficient distance away from the samples that
25 the samples can be contacted by plasma species without being inside the plasma discharge
26 area. After O₂ plasma exposure was begun, water gas was dosed into the chamber and
27 eventually displaced the oxygen. The water was added to form -OH surface terminations

1 on the substrate surface. The coating was applied by first admitting water vapor to the
2 chamber until the pressure in the chamber exceeded 5 Torr. Subsequently, the chamber
3 was evacuated down to the desired water vapor pressure between 1 and 1.3 Torr. Next a
4 dimethyldichlorosilane (DDMS) precursor was introduced into the process chamber until
5 the total pressure was in the range of 2.5 - 3 Torr. The reaction was carried out for 10 - 15
6 minutes, after which time the chamber was pumped out and vented with nitrogen. It was
7 concluded that increasing substrate temperature during coating over a range of 20 °C to
8 50 °C, all other variables being equal, results in films that have decreasing water contact
9 angle. The main result of the temperature experiments is said to be that there is no need
10 to heat the sample. In a second article entitled: "Vapor Deposition of Amino-
11 Functionalized Self-Assembled Monolayers on Mems", Reliability, Testing, and
12 Characterization of MEMS MOEMS II", Rajeshuni Ramesham, Danelle M. Tanner,
13 Editors, Proceedings of SPIE Vol. 4980 (2003), authors Matthew G. Hankins et al.
14 describe microengine test devices coated with films made from amino-functionalized
15 silanes. The coatings were applied in a vapor-deposited self-assembled monolayer system
16 developed at Sandia National Laboratories. The process variables used to deposit the
17 coatings are not discussed in the article.

18 [0015] U.S. Patent No. 6,576,489 to Leung et al., issued June 10, 2003 describes
19 methods of forming microstructure devices. The methods include the use of vapor-phase
20 alkylsilane-containing molecules to form a coating over a substrate surface. The
21 alkylsilane-containing molecules are introduced into a reaction chamber containing the
22 substrate by bubbling an anhydrous, inert gas through a liquid source of the alkylsilane-
23 containing molecules, to transport the molecules in the vapor phase into the reaction
24 chamber. The formation of the coating is carried out on a substrate surface at a
25 temperature ranging between about 15 °C and 100 °C, at a pressure in the reaction
26 chamber which is said to be below atmospheric pressure, and yet sufficiently high for a
27 suitable amount of alkylsilane-containing molecules to be present for expeditious

1 formation of the coating. The liquid source of alkylsilane molecules may be heated to
2 increase the vapor pressure of the alkylsilane-containing molecules.

3 [0016] While various methods useful in applying layers and coatings to semiconductor
4 devices and MEMS have been discussed above and there is some description of the kinds
5 of apparatus which may be employed to deposit the coatings, the apparatus description is
6 minimal. The following references deal more with apparatus. U.S. Patent Application
7 Publication No. US 2001/0028924 A1 of Arthur Sherman, published October 11, 2001,
8 pertains to a method of sequential chemical vapor deposition which is used to deposit
9 layers of inorganic materials such as SiO_x , Al_2O_3 , TiO_2 , Si_3N_4 , SiO_xN_y , and aluminum
10 films doped with copper and silicon. U.S. Patent Application Publication No. US
11 2002/0076507 A1 of Chiang et al., published June 20, 2002, describes an atomic layer
12 deposition (ALD) process based on the sequential supply of at least two separate reactants
13 into a process chamber. A first reactant reacts (becomes adsorbed) with the surface of the
14 substrate via chemisorption. The first reactant gas is removed from the process chamber,
15 and a second reactant gas reacts with the adsorbed reactant to form a monolayer of the
16 desired film. The process is repeated to form a layer of a desired thickness. To reduce the
17 process time, there is no separate purge gas used to purge the first reactant gas from the
18 chamber prior to introducing the second gas, containing the second reactant. Instead, the
19 purge gas also includes the second reactant. Several valving systems for gas flow to
20 provide various mixtures of gases are described in detail.

21 [0017] The background information above provides a number of methods for
22 generation of coatings which have considerable commercial applicability. The apparatus
23 described for producing layers or coatings for use in electronic devices and /or micro-
24 electromechanical systems devices enables application of the layers or coatings, but does
25 not provide sufficient accuracy and repeatability in terms of the amount of the vaporous
26 reactants provided to the substrate surface. As a result, the precise composition of the
27 layer or coating which is desired may not be available. At other times, because of the

1 improper ratio of various reactants relative to each other, or oversaturation by a precursor,
2 reactants may polymerize and/or particulate agglomerations may be formed which act as
3 surface contaminants. Further, the ability to reproduce the same coating reliably, time
4 after time, is diminished due to lack of control over the precise amount of reactants
5 supplied to the coating formation process. This decreases the product yield and affects
6 the commercial viability of a coating process. It would be highly desirable to have a more
7 accurate and reliable method of supplying precise quantities of the reactants to the process
8 chamber and to the substrate surface for coating formation.

9 [0018] **SUMMARY OF THE INVENTION**

10 [0019] We have developed an improved vapor-phase deposition method and apparatus
11 for the application of layers and coatings on substrates. The method and apparatus are
12 useful in the fabrication of electronic devices, micro-electromechanical systems (MEMS),
13 Bio-MEMS devices, and microfluidic devices. The coating formation method employs a
14 batch-like addition and mixing of all of the reactants to be consumed in a coating
15 formation process. The coating formation process may be complete after one step, or may
16 include a number of individual steps, where different or repetitive reactive processes are
17 carried out in each individual step. The apparatus used to carry out the method provides
18 for the addition of a precise amount of each of the reactants to be consumed in a single
19 reaction step of the coating formation process. The apparatus may provide for precise
20 addition of quantities of different combinations of reactants during a single step or when
21 there are a number of different individual steps in the coating formation process. The
22 precise addition of each of the reactants is based on a metering system where the amount
23 of reactant added in an individual step is carefully controlled. In particular, the reactant in
24 vapor form is metered into a vapor reservoir with a predetermined set volume at a
25 specified temperature to a specified pressure to provide a highly accurate amount of
26 reactant. The entire measured amounts(s) of each reactant is (are) transferred in batch

1 fashion into the process chamber in which the coating is formed. The order in which
2 each reactant is added to the chamber for a given reaction step is selectable, and may
3 depend on the relative reactivities of the reactants when there are more than one reactant,
4 the need to have one reactant or the catalytic agent contact the substrate surface first, or a
5 balancing of these considerations.

6 [0020] In some instances, it may be necessary to carry out a series of individual vapor
7 delivery steps to provide a complete coating, rather than carrying out one continuous
8 reaction process. For example, all of a precisely measured quantity of one reacting
9 component may be added initially, followed by a series of precisely measured quantities
10 of a second reacting component. In each case all of the measured quantity is added to the
11 reaction chamber. This provides a precise, carefully measured quantity of reactant at a
12 precise time for each reactant.

13 [0021] A computer driven process control system may be used to provide for a series
14 of additions of reactants to the process chamber in which the layer or coating is being
15 formed. This process control system typically also controls other process variables, such
16 as, (for example and not by way of limitation), process time, chamber pressure,
17 temperatures of the process chamber and the substrate to which the coating is applied, as
18 well as temperatures of the vapor delivery lines and vapor reservoirs relative to the
19 temperatures of the precursors.

20 [0022] The apparatus for vapor deposition of coatings is particularly useful for
21 deposition of coatings having a thickness ranging from about 5 Å to about 1,000 Å, (and
22 may be used for increased coating thicknesses), where at least one precursor used for
23 formation of the coating exhibits a vapor pressure below about 150 Torr at a temperature
24 of 25 °C. The apparatus includes at least one precursor container in which at least one
25 precursor, in the form of a liquid or solid, is placed; at least one precursor vapor reservoir
26 for holding vapor of the at least one precursor; at least one device which controls
27 precursor vapor flow from the precursor container into the precursor vapor reservoir; a

1 pressure sensor in communication with the precursor vapor reservoir; a process controller
2 which receives data from the pressure sensor, compares the data with a desired nominal
3 vapor reservoir pressure, and sends a signal to a device which controls vapor flow from
4 the precursor container into the precursor vapor reservoir, to prevent further vapor flow
5 into the precursor vapor reservoir when the desired nominal pressure is reached; a device
6 which controls precursor vapor flow into the precursor vapor reservoir upon receipt of a
7 signal from the process controller; a process chamber for vapor deposition of the coating
8 on a substrate present in the process chamber; and a device which controls precursor
9 vapor flow into the process chamber upon receipt of a signal from the process controller.

10 [0023] In some instances, the apparatus includes a device which applies heat to the
11 precursor while it is in the container, to produce a vaporous phase of the precursor.

12 Typically the apparatus includes at least one catalyst container, in which a catalyst, in the
13 form of a liquid or a solid is placed; and a catalyst vapor reservoir for holding vapor of the
14 catalyst, with the same basic elements facilitating transfer of catalyst to the process
15 chamber at those described with reference to a precursor.

16 [0024] A method of the invention provides for vapor-phase deposition of coatings,
17 where at least one precursor used for formation of the coating exhibits a vapor pressure
18 below about 150 Torr at a temperature of 25 °C. The method includes the steps of: a)
19 providing a processing chamber in which the coating is vapor deposited; b) providing at
20 least one precursor exhibiting a vapor pressure below about 150 Torr at a temperature of
21 25 °C; c) transferring vapor of the precursor to a precursor vapor reservoir in which the
22 precursor vapor accumulates; d) accumulating a nominal amount of the precursor vapor
23 required for the vapor phase coating deposition; and e) adding the nominal amount of the
24 precursor vapor to the processing chamber in which the coating is being deposited.

25 Typically at least one catalyst vapor is added to the process chamber in addition to the at
26 least one precursor vapor, where the relative quantities of catalyst and precursor vapors
27 are based on the physical characteristics to be exhibited by the coating.

1 [0025] **BRIEF DESCRIPTION OF THE DRAWINGS**

2 [0026] Figure 1 shows a cross-sectional schematic of an apparatus 100 for vapor
3 deposition of a coating, which apparatus employs the present invention for metering
4 precise amounts of reactants to the coating formation process.

5 [0027] Figure 2 shows a cross-sectional schematic view of an apparatus 200 of the
6 kind shown in Figure 1, where a number of substrates are processed simultaneously.

7 [0028] Figure 3 is a schematic illustrating a system 300 of the kind which could be
8 used for production of a MEMS device where there are moving parts which are formed by
9 a release-etching process in system 304 and where, subsequent to the release-etch process,
10 the MEMS device is transferred through a pressure controlled passageway 306 to a
11 coatings application chamber 302 of the kind described with reference to Figure 1.

12 [0029] **DETAILED DESCRIPTION OF EXEMPLARY EMBODIMENTS**

13 [0030] As a preface to the detailed description, it should be noted that, as used in this
14 specification and the appended claims, the singular forms "a", "an", and "the" include
15 plural referents, unless the context clearly dictates otherwise.

16 [0031] We have developed an improved vapor-phase deposition method and apparatus
17 for application of a thin (typically 5 Å to 1,000 Å thick, in and in some instances up to
18 about 2,000 Å thick) film or coating to a semiconductor device substrate or a micro-
19 electromechanical systems device. The method and apparatus are employed when at least
20 one of the reactants or a catalyst used in coating formation must be vaporized prior to use,
21 and where the amount of each reactant must be carefully controlled in terms of quantity
22 available to react, in terms of time available for reaction at a given process pressure, or a
23 combination of both. The method is particularly useful in the deposition of thin films or
24 coatings where the thickness of the film or coating ranges from about 5 Å to about 500 Å,

1 and provides excellent results for coatings having a thickness in the range of about 300 Å.
2 [0032] As previously discussed herein, there are a multitude of applications for such
3 thin layers or coatings. For purposes of illustration, applicants will describe the method
4 and apparatus of the present invention in terms of the tunable deposition of an organic
5 monolayer; however, one skilled in the art of deposition of layers and coatings will be
6 able to use the concepts described for coatings which are not organic, and/or not
7 monolayers.

8 [0033] There is a particular interest at this time in anti-stiction layers and coatings
9 which are needed to enable reliable, long-term performance of the micro-
10 electromechanical systems. Stiction (adhesion) of compliant micromechanical parts is
11 one of the key reliability issues that has proven difficult to overcome. Conventionally,
12 solution-based antistiction monolayers have been used; however, more recently, due to
13 capillary stiction, particulation problems, and unsatisfactory quality, scalability, and
14 reproducibility of the films produced by relatively lengthy wet processing, efforts are
15 underway to develop vapor deposition methods for the antistiction coatings. The vacuum
16 processing and vapor phase deposition of antistiction coatings, including self-assembled
17 monolayers (SAMs) has provided higher quality films in general. An integrated vapor
18 deposition process (including surface plasma treatment in the same chamber) typically
19 offers better control of surface reactivity, while avoiding the potential for stiction between
20 micromechanical parts during application of the antistiction coating.

21 [0034] The embodiments described in the examples below are with reference to the
22 application of organic SAM coatings which are applied using vapor deposition techniques
23 over the surface of a single crystal silicon substrate. The apparatus used for deposition of
24 the coatings is available from Applied Microstructures, Inc. of San Jose, California. This
25 apparatus is specifically designed to provide a high degree of control in terms of quantity
26 of reactants provided to the coating application processing chamber for each individual
27 process step, and in terms of the time and order at which these reactants are made

1 available for the reaction.

2 [0035] The properties of the deposited films were evaluated using standard surface
3 analysis methods, cantilever-beam-array test structures, and performance analysis of
4 working MEMS devices.

5
6 [0036] I. AN APPARATUS FOR VAPOR DEPOSITION OF THIN COATINGS

7 [0037] Figure 1 shows a cross-sectional schematic of an apparatus 100 for vapor
8 deposition of thin coatings. The apparatus 100 includes a process chamber 102 in which
9 thin (typically 5 Å to 1,000Å thick) coatings are vapor deposited. A substrate 106 to be
10 coated rests upon a substrate holder 104, typically within a recess 107 in the substrate
11 holder 104. Depending on the chamber design, the substrate 106 may rest on the chamber
12 bottom (not shown in this position in Figure 1). Attached to process chamber 102 is a
13 remote plasma source 110, connected via a valve 108. Remote plasma source 110 may be
14 used to provide a plasma which is used to clean and/or convert a substrate surface to a
15 particular chemical state prior to application of a coating (which enables reaction of
16 coating species and/or catalyst with the surface, thus improving adhesion and/or
17 formation of the coating); or may be used to provide species helpful during formation of
18 the coating (not shown) or modifications of the coating after deposition. The plasma may
19 be generated using a microwave, DC, or inductive RF power source, or combinations
20 thereof. The process chamber 102 makes use of an exhaust port 112 for the removal of
21 reaction byproducts and is opened for pumping/purging the chamber 102. A shut-off
22 valve or a control valve 114 is used to isolate the chamber or to control the amount of
23 vacuum applied to the exhaust port. The vacuum source is not shown in Figure 1.

24 [0038] The apparatus 100 shown in Figure 1 is illustrative of a vapor deposited coating
25 which employs two precursor materials and a catalyst. One skilled in the art will
26 understand that one or more precursors and from zero to multiple catalysts may be used
27 during vapor deposition of a coating. A catalyst storage container 116 contains catalyst

1 154, which may be heated using heater 118 to provide a vapor, as necessary. It is
2 understood that precursor and catalyst storage container walls, and transfer lines into
3 process chamber 102 will be heated as necessary to maintain a precursor or catalyst in a
4 vaporous state, minimizing or avoiding condensation. The same is true with respect to
5 heating of the interior surfaces of process chamber 102 and the surface of substrate 106 to
6 which the coating (not shown) is applied. A control valve 120 is present on transfer line
7 119 between catalyst storage container 116 and catalyst vapor reservoir 122, where the
8 catalyst vapor is permitted to accumulate until a nominal, specified pressure is measured
9 at pressure indicator 124. Control valve 120 is in a normally-closed position and returns
10 to that position once the specified pressure is reached in catalyst vapor reservoir 122. At
11 the time the catalyst vapor in vapor reservoir 122 is to be released, valve 126 on transfer
12 line 119 is opened to permit entrance of the catalyst present in vapor reservoir 122 into
13 process chamber 102 which is at a lower pressure. Control valves 120 and 126 are
14 controlled by a programmable process control system of the kind known in the art (which
15 is not shown in Figure 1).

16 [0039] A Precursor 1 storage container 128 contains coating reactant Precursor 1,
17 which may be heated using heater 130 to provide a vapor, as necessary. As previously
18 mentioned, Precursor 1 transfer line 129 and vapor reservoir 134 internal surfaces are
19 heated as necessary to maintain a Precursor 1 in a vaporous state, avoiding condensation.
20 A control valve 132 is present on transfer line 129 between Precursor 1 storage container
21 128 and Precursor 1 vapor reservoir 134, where the Precursor 1 vapor is permitted to
22 accumulate until a nominal, specified pressure is measured at pressure indicator 136.
23 Control valve 132 is in a normally-closed position and returns to that position once the
24 specified pressure is reached in Precursor 1 vapor reservoir 134. At the time the
25 Precursor 1 vapor in vapor reservoir 134 is to be released, valve 138 on transfer line 129
26 is opened to permit entrance of the Precursor 1 vapor present in vapor reservoir 134 into
27 process chamber 102, which is at a lower pressure. Control valves 132 and 138 are

1 controlled by a programmable process control system of the kind known in the art (which
2 is not shown in Figure 1).

3 [0040] A Precursor 2 storage container 140 contains coating reactant Precursor 2,
4 which may be heated using heater 142 to provide a vapor, as necessary. As previously
5 mentioned, Precursor 2 transfer line 141 and vapor reservoir 146 internal surfaces are
6 heated as necessary to maintain Precursor 2 in a vaporous state, avoiding condensation.
7 A control valve 144 is present on transfer line 141 between Precursor 2 storage container
8 146 and Precursor 2 vapor reservoir 146, where the Precursor 2 vapor is permitted to
9 accumulate until a nominal, specified pressure is measured at pressure indicator 148.
10 Control valve 141 is in a normally-closed position and returns to that position once the
11 specified pressure is reached in Precursor 2 vapor reservoir 146. At the time the
12 Precursor 2 vapor in vapor reservoir 146 is to be released, valve 150 on transfer line 141
13 is opened to permit entrance of the Precursor 2 vapor present in vapor reservoir 146 into
14 process chamber 102, which is at a lower pressure. Control valves 144 and 150 are
15 controlled by a programmable process control system of the kind known in the art (which
16 is not shown in Figure 1).

17 [0041] During formation of a coating (not shown) on a surface 105 of substrate 106, at
18 least one incremental addition of vapor equal to the vapor reservoir 122 of the catalyst
19 154, or the vapor reservoir 134 of the Precursor 1, or the vapor reservoir 146 of Precursor
20 2 may be added to process chamber 102. The total amount of vapor added is controlled
21 by both the adjustable volume size of each of the expansion chambers (typically 50 cc up
22 to 1,000 cc) and the number of vapor injections (doses) into the reaction chamber.
23 Further, the process control system (not shown) may adjust the set pressure 124 for
24 catalyst vapor reservoir 122, or the set pressure 136 for Precursor 1 vapor reservoir 134,
25 or the set pressure 148 for Precursor 2 vapor reservoir 146, to adjust the amount of the
26 catalyst or reactant added to any particular step during the coating formation process.
27 This ability to fix precise amounts of catalyst and coating reactant precursors dosed

1 (charged) to the process chamber 102 at any time during the coating formation enables the
2 precise addition of quantities of precursors and catalyst at precise timing intervals,
3 providing not only accurate dosing of reactants and catalysts, but repeatability in terms of
4 time of addition.

5 [0042] This apparatus provides a very inexpensive, yet accurate method of adding
6 vapor phase precursor reactants and catalyst to the coating formation process, despite the
7 fact that many of the precursors and catalysts are typically relatively non-volatile
8 materials. In the past, flow controllers were used to control the addition of various
9 reactants; however, these flow controllers may not be able to handle some of the
10 precursors used for vapor deposition of coatings, due to the low vapor pressure and
11 chemical nature of the precursor materials. The rate at which vapor is generated from
12 some of the precursors is generally too slow to function with a flow controller in a manner
13 which provides availability of material in a timely manner for the vapor deposition
14 process.

15 [0043] The present apparatus allows for accumulation of the vapor into an adequate
16 quantity which can be charged (dosed) to the reaction. In the event it is desired to make
17 several doses during the progress of the coating deposition, the apparatus can be
18 programmed to do so, as described above. Additionally, adding of the reactant vapors
19 into the reaction chamber in controlled aliquots (as opposed to continuous flow) greatly
20 reduces the amount of the reactants used and the cost of the coating process.

21 [0044] Figure 2 shows a cross-sectional schematic of an embodiment of a vapor
22 deposition processing apparatus 200 which provides for the application of a thin coating to
23 a plurality of substrates 206 simultaneously. The apparatus 200 includes a process chamber
24 202 in which thin (5 Å to 1,000 Å thick) coatings are vapor deposited. A plurality of
25 substrates 206 to be coated rest upon a substrate holder 204, which can be moved within
26 process chamber 202 using a device 209. Attached to process chamber 202 is a remote
27 plasma source 210, connected via a valve 208. Remote plasma source 210 may be used to

1 provide a plasma which is used to clean or to react with (activate) a substrate surface prior
2 to application of a coating or may be used to provide species helpful during or after formation
3 of the coating (not shown). As previously described, the plasma may be generated using a
4 microwave, DC, or inductive RF power source, or may be generated using a combination of
5 power sources. The process chamber 202 makes use of an exhaust port 212 for the removal
6 of reaction byproducts and for pumping/purging of the process chamber 202. A control valve
7 214 is used to control the speed of vacuum pumping and evacuation (vacuum generator not
8 shown).

9 [0045] The apparatus 200 shown in Figure 2 is illustrative of a vapor deposited coating
10 which employs two precursor materials and a catalyst. One skilled in the art will
11 understand that one or more precursors and from zero to multiple catalysts may be used
12 during vapor deposition of a coating. Catalyst for use during the coating deposition
13 process enters process chamber 202 from a catalyst vapor reservoir (not shown) through
14 line 219 through control valve 220. Precursor 1 for use during the coating deposition
15 process enters process chamber 202 from a Precursor 1 vapor reservoir (not shown)
16 through line 217 through control valve 218, and Precursor 2 enters process chamber 202
17 from a Precursor 2 vapor reservoir (not shown) through line 215 through control valve
18 216. As previously mentioned transfer lines for the Catalyst, Precursor1, and Precursor 2
19 are heated as necessary to maintain these materials in a vaporous state, avoiding
20 condensation. The Catalyst, Precursor 1 and Precursor 2 may be distributed within
21 process chamber 202 through a baffling system 205 which typically contains separate
22 distribution paths for the catalyst and each precursor used in the coating deposition
23 process. The baffling system helps ensure even distribution of each reaction component
24 material throughout process chamber 202. Process chamber 202 typically uses a swing
25 door or a load lock 226. Upon completion of the reaction, process byproducts exit
26 process chamber 202 through exhaust port 212, which is connected to a vacuum pump
27 (not shown). The interior surfaces of process chamber 200 and other apparatus such as

1 baffling system 205 are typically heated to prevent condensation of the Catalyst, Precursor
2 1, and Precursor 2 upon these apparatus surfaces. The reaction pressure is typically
3 determined by the amount of reactants injected into chamber 202. The processing
4 chamber pressure is monitored by pressure sensing device 224, which is coordinated with
5 the vapor delivery system previously described through a computerized control system
6 (not shown). A flow control valve 214 is used to remove vapor and byproducts in general
7 from the interior of process chamber 202. The operation of flow control valve 214 may
8 be coordinated, through the computerized control system, to function in combination with
9 the pressure sensing device, to maintain the desired pressure during pumping/purging
10 steps.

11 [0046] Figure 3 shows a cross-sectional schematic of a MEMS processing system 300
12 which employs a release-etch processing chamber 310 (of the type used to produce
13 moveable elements of a mechanical nature in a MEMS device) and a vapor deposition
14 coating application system 312 of the kind previously described with reference to Figures
15 1 and 2. The release-etch process chamber 310 includes apparatus for reagent entry 324
16 (shown as a single line for convenience, but which may be a plurality of lines); a pressure
17 sensing and monitoring device 326; an exhaust port 334, with flow control valve 332; a
18 recirculation loop 331 with pump 330 is optional, but can be used to provide important
19 processing advantages. The vapor deposition coating apparatus process chamber 308
20 includes apparatus for reagent (catalyst and precursor) entry 312 (shown as a single line
21 for convenience, but which is a plurality of lines as previously discussed); a pressure
22 sensing and monitoring device 314; and an exhaust port 322, with a control valve 320.
23 The release-etch process chamber 310 and vapor deposition coating process chamber 308
24 are joined to each other through an isolation valving system 306.

25 [0047] II. EXEMPLARY METHODS OF THE INVENTION :

26 [0048] As discussed with respect to the apparatus, there have been problems in

1 providing accurately measured quantities of reactants on a repeatable basis to a vapor
2 deposition coating system. This is because many of the precursor materials for coating
3 formation have a low vapor pressure or are not compatible with mass flow controllers. In
4 addition, for many of the vapor deposition coatings, water acts as a catalyst to the coating
5 formation, and the amount of water present in the coating deposition chamber is not
6 precisely controlled.

7 [0049] When the surfaces of features to be coated are in the nanometer size range, it is
8 critical that the coating deposition be carefully controlled to provide the desired thickness
9 of coating (typically about 5 Å to 1,000 Å, and in some instances up to 2,000 Å) over the
10 entire surface area, and that there be no formation of particulate or agglomerations within
11 the depositing coating. In order to meet these critical requirements for thin vapor
12 deposited coatings, it is necessary to provide accurately measured quantities of reactants
13 and catalysts and to control the time period over which these accurately measured
14 quantities are delivered to the surface of the substrate or the deposition chamber.
15 Delivery to the surface of the substrate depends on interior design of the processing
16 chamber, and there are techniques which are well known in the art of chemical vapor
17 deposition which apply to delivery of reagents to the substrate surface. The present
18 method addresses the problem of providing accurately measured quantities of reactants
19 and catalysts which are delivered in the proper order and at the proper time to the coating
20 deposition chamber.

21 [0050] By way of example and not by way of limitation, the provision of accurate
22 quantities of reactants and catalysts will be illustrated with respect to monolayer coatings
23 of chloro-silanes and alkyl-silanes which are used in many applications such as MEMS,
24 BioMEMS, and micro-fluidics. Organic precursor materials such as (and not by way of
25 limitation) silanes, chlorosilanes, fluorosilanes, methoxy silanes, alkyl silanes, and amino
26 silanes are useful in general. Some of the particular precursors used to produce coatings
27 are, by way of example and not by way of limitation, perfluorodecyltrichlorosilanes

(FDTS), undecenyltrichlorosilanes (UTS), vinyl-trichlorosilanes (VTS), decyltrichlorosilanes (DTS), octadecyltrichlorosilanes (OTS), dimethyldichlorosilanes (DDMS), dodecenyltrichlorosilanes (DDTS), fluoro-tetrahydrooctyldimethylchlorosilanes (FOTS), perfluorooctyldimethylchlorosilanes, aminopropylmethoxysilanes (APTMS), fluoropropylmethyldichlorosilanes, and perfluorodecyldimethylchlorosilanes. The OTS, DTS, UTS, VTS, DDTS, FOTS, and FDTS are all trichloro silane precursors. The other end of the precursor chain is a saturated hydrocarbon with respect to OTS, DTS, and UTS; contains a vinyl functional group, with respect to VTS and DDTS; and contains fluorine atoms with respect to FDTS (which also has fluorine atoms along the majority of the chain length). Other useful precursors include 3-aminopropyltrimethoxysilane (APTMS), which provides amino functionality, and 3-glycidoxypropyltrimethoxysilane (GPTMS). One skilled in the art of organic chemistry can see that the vapor deposited coatings from these precursors can be tailored to provide particular functional characteristics for a coated surface. The surface to be coated may be silicon, glass, organic (plastic) or metal, for example.

[0051] Most of the silane-based precursors, such as commonly used di- and tri-chlorosilanes, for example and not by way of limitation, tend to create agglomerates on the surface of the substrate during the coating formation. These agglomerates can cause structure malfunctioning or stiction. Such agglomerations are produced by partial hydrolysis and polycondensation of the polychlorosilanes. This agglomeration can be prevented by precise metering of moisture in the process ambient which is a source of the hydrolysis, and by carefully controlled metering of the availability of the chlorosilane precursors to the coating formation process.

[0052] Those working in the MEMS field have recognized the advantages of vapor deposited coatings over coatings applied using liquid-based immersion, spray-on and spin-on techniques. Some of those advantages include: elimination of stiction induced by capillary forces; control of the coating environment (particularly the amount of moisture

1 present); uniform coating properties on micron and nanometer size patterns such as
2 microchannels and pores; solvent free process with no contamination; and, a faster
3 process which is compatible with MEMS clean room processing protocols, for example.

4 [0053] In a vapor deposition process which employs one precursor and a catalyst, a
5 DDTS precursor may be used in combination with a water catalyst, for example. In a
6 vapor deposition process which employs two precursors and a catalyst, a DDTS
7 precursor, a UTS precursor, and a water catalyst may be used in combination, for example
8 and not by way of limitation. The relative quantities of the DDTS and UTS precursors
9 can be adjusted to provide different overall functional properties for the coated surface.
10 However, the ability to control the coated surface properties and to reliably reproduce the
11 properties depends on the ability to control the relative quantities of the DDTS and UTS
12 precursors supplied to the coating formation process. This ability depends on provision of
13 accurately controlled quantities of the kind which are possible when the present method of
14 invention is used.

15 [0054] When the precursors used to form the initial vapor deposited coating have
16 potentially reactive functional groups on the exposed surface of the coating, there
17 functional groups can be further reacted with other chemical compounds to modify the
18 functionality of the surface of the coating.

19 [0055] In addition to organo-silanes, poly(ethylene glycol) (PEG) is used separately or
20 in combination with other film-forming compounds such as the silanes to provide
21 biotechnology functional surfaces. One portion of the coated surface may be coated with
22 the reaction product of an organo-silane, while another is coated with a PEG reaction
23 product. In the alternative, the organo-silane may include a functional group on the distal
24 end of the polymer chain, away from the substrate surface, which functional group can be
25 reacted with a PEG reactant, to place a PEG functional group at the distal end of the
26 polymer chain, affecting coating surface functionality. For example, PEG films are
27 known to reduce protein adsorption in micro-fluidic applications. PEG 3 films include 6

1 carbons, while PEG 2 films include 4 carbons. The length of the polymer chain can also
2 be adjusted to provide the desired film properties.

3 [0056] The present method for vapor deposition of coatings provides a number of
4 advantages. Typically a remote plasma source is used to generate a cleaning plasma
5 (typically oxygen-containing) which can be used to remove contaminants from the
6 substrate surface. When the substrate is silicon, the cleaning process is useful in the
7 formation of -OH functional groups which serve as binding sites for a number of coating
8 precursors such as the trichloro silanes. Precise control of the amount of precursors is
9 ensured through the direct measurement of the vapor pressure of the precursor at a given
10 temperature in a known volume. Process control is provided by varying the partial
11 pressure and the amount of the precursors employed in the vapor phase reaction.

12
13 [0057] III. GENERAL PARAMETER DESCRIPTIONS FOR VAPOR
14 DEPOSITION OF A MOLECULAR COATING:

15 [0058] Surfaces to be coated are typically pretreated in the same chamber. To obtain
16 bonding of a chloro- functional group to a substrate surface, it is necessary to create OH-
17 terminated sites on the surface. This can be done in the deposition chamber by treating a
18 silicon surface with an oxygen plasma in the presence of moisture. The plasma may be
19 produced using a remote power source of the kind previously described. The pressure in
20 the processing chamber during exposure of a substrate to the oxygen plasma typically
21 ranges from about 0.2 Torr to about 2 Torr, more typically from about 0.5 Torr to about 1
22 Torr. For a process chamber having a volume of about 2 liters, the plasma source gas
23 oxygen flow rate ranges from about 50 sccm to about 300 sccm, more typically from
24 about 100 sccm to 200 sccm. The substrate processing time is typically about 1 minute to
25 about 10 minutes, and more typically from about 1 minute to about 5 minutes.

26 [0059] The coating deposition is typically carried out in the deposition chamber at a
27 pressure ranging from about 100 mTorr to about 10 Torr, more typically at a pressure

1 ranging from about 0.5 Torr to about 5 Torr, and most typically at a pressure ranging from
2 about 0.1 Torr to about 3 Torr. The deposition temperature of the substrate depends on
3 the particular coating precursors and on the substrate material. For a silicon substrate,
4 where the coating precursor is FOTS or DDMS, used in combination with a water
5 catalyst, the substrate temperature is typically in the range of about 20 °C to about 60 °C.
6 To maintain these coating precursors in a vaporous state prior to reaction, the interior
7 surfaces of the coating deposition process chamber are typically maintained at a
8 temperature ranging from about 30 °C to about 60 °C. The time period required to
9 produce a continuous monolayer coating over the entire surface of the silicon substrate
10 using these coating precursors and the specified reaction temperature ranges from about 1
11 minute to about several hours, depending on precursor chemistry and substrate material,
12 typically the reaction time period is in the range of 5 minutes to 30 minutes, where the
13 coating precursor is FOTS or DDMS.

14 [0060] For deposition of an antistiction MEMS coating from chlorosilane precursors,
15 the following recipe and process conditions were used. In each case, a single precursor,
16 selected from the group consisting of dimethyldichlorosilane (DDMS), tridecafluoro-
17 1,1,2,2-tetrahydrooctyltrichlorosilane (FOTS), and heptadecafluoro-1,1,2,2-
18 tetrahydrodecyltrichlorosilane (FDTs), was vaporized and used in combination with water
19 vapor as a catalyst. In each instance, the precursor and the water were degassed under
20 vacuum to remove dissolved gases prior to introduction into the system. The conditions
21 for degassing vary, depending on the precursor and catalyst, but one skilled in the
22 art can easily determine proper degassing conditions.

23 [0061] With reference to Figure 1, the degassed water was placed in catalyst storage
24 container 116 and was heated to a temperature of about 30 °C to produce a vapor which
25 was passed through transfer line 119 to accumulate in vapor reservoir 122, which had a
26 volume of 300 cc, and which was held at a pressure of 16 Torr. A DDMS precursor was
27 placed in Precursor 1 storage container 128 and was heated to a temperature of 30 °C to

1 produce a vapor which was passed through transfer line 129 to accumulate in vapor
2 reservoir 134, which had a volume of 50 cc, and which was held at a pressure of 50 Torr.
3 There was no precursor in Precursor 2 storage container 140.

4 [0062] A silicon substrate 106, having a surface 105 was manually loaded onto the
5 substrate holder 104. The process chamber 102, having a volume of about 2 liters, was
6 pumped down to about 20 mTorr and purged with nitrogen gas prior to and after the
7 coating reaction, which consisted of oxygen plasma treatment followed by coating
8 deposition. The process chamber 102 was vented to atmosphere. The process chamber
9 102 was then purged using nitrogen (filled with nitrogen to 10 Torr/pumped to 0.7 Torr,
10 five times). The surface 105 was treated with a remotely generated oxygen plasma from
11 plasma source 110 in the manner described above. Oxygen was directed into a plasma
12 generation source 110 through a mass flow controller (not shown). The oxygen flow rate
13 for plasma generation, based on the desired plasma residence time for process chamber
14 102, was about 200 sccm. The pressure in process chamber 102 was about 0.6 Torr.
15 The surface 105 of silicon substrate 106 was treated with the oxygen plasma at a pressure
16 of about 0.6 Torr for a time period of about 5 minutes. The plasma treatment was
17 discontinued, and the process chamber 102 was pumped down to the base pressure of
18 about 30 mTorr.

19 [0063] The water vapor reservoir 122 was charged with water vapor to a pressure of 16
20 Torr, as described above. The valve 126 between water vapor reservoir 122 and process
21 chamber 102 was opened until both pressures equalized (a time period of about 5
22 seconds) to about 0.8 Torr. The water vapor reservoir 122 was charged with vapor to 16
23 Torr a second time, and this volume of vapor was also dumped into the process chamber,
24 bringing the total water vapor pressure in process chamber 102 to about 1.6 Torr. The
25 DDMS vapor reservoir 134 had been charged with the precursor vapor to 50 Torr, as
26 described above, and the DDMS vapor was added immediately after completion of the
27 water vapor addition. The valve 138 between the DDMS vapor reservoir 134 and

1 process chamber 102 was opened until both pressures were equalized (a time period of
2 about 5 seconds) to about 4Torr. The water and DDMS vapors were maintained in
3 process chamber 102 for a time period of 15 minutes. The process chamber was then
4 pumped back to the base pressure of about 30 mTorr.

5 [0064] The process chamber 102 was then purged (filled with nitrogen to
6 10Torr/pumped to 0.7 Torr) five times. The process chamber was then vented to
7 atmosphere, and the silicon substrate 106 was manually removed from the process
8 chamber.

9 [0065] The resulting coated surface is typically very hydrophobic, as measured by
10 water contact angle, which is typically about 103 ° for DDMS films. The surface was
11 particularly smooth, having an RMS of 0.2 nm, with no visible particulation or defects.
12 The measured work of adhesion was reduced up to 3,000 times depending on the specific
13 process/chemistry. Under the conditions provided above, the measured work of adhesion
14 was reduced to about 30 μJ^{-2} . The properties of the vapor deposited films are equivalent
15 to or better than those reported for liquid-phase deposited films. In addition, use of vapor
16 deposition prevents the stiction which frequently occurs during wet processing of the
17 substrate.

18 [0066] The above described exemplary embodiments are not intended to limit the
19 scope of the present invention, as one skilled in the art can, in view of the present
20 disclosure expand such embodiments to correspond with the subject matter of the
21 invention claimed below.